⑫ # EUROPEAN PATENT APPLICATION

�54 Drilling fluid.

�57 A drilling fluid comprising:
a) at least one polymeric viscosifier
b) at least one polymeric fluid loss reducer
c) at least one high molecular weight organic polycationic polymeric coagulant and/or flocculant.
The objective of the present invention is to assess the possibilities of coagulants or flocculants for the improvement of solids removal from the drilling fluid.

EP 0 175 412 A2

DRILLING FLUID

The invention relates to a drilling fluid comprising:

a)   at least one polymeric viscosifier

b)   at least one polymeric fluid loss reducer

c)   at least one high molecular weight organic polycationic
polymeric coagulant and/or flocculant.

In this application by a high molecular weight is meant a
molecular weight in the range from 500,000 to 15,000,000.

When drilling subterranean wells such as, for example, oil
or gas wells, the rotary drilling method is commonly employed.
The rotary drilling method utilizes a bit attached to a drill
stem, and a drilling fluid or "mud" which is circulated through
the drill stem to the bottom of the borehole where it is ejected
through small openings in the drill bit. The fluid is then
returned to the surface through the annular space between the
drill stem and the borehole wall, or casing if one has been
installed. Upon reaching the surface, the drilling fluid or
"mud" is ordinarily treated to remove cuttings obtained from the
borehole, and is then recirculated.

Drilling fluids serve many functions, and should therefore
possess a number of desirable physical and rheological proper-
ties. For example, the viscosity of a drilling fluid should be
sufficient to permit it to effectively transport bit cuttings
from the bottom of the borehole to the surface for removal. A
drilling fluid should also prevent excessive amounts of fluid
from flowing from the borehole into surrounding formations by
depositing on the wall of the hole a thin but substantially
impervious filter cake. In addition, a drilling fluid should be

able to hold solids in suspension, preventing their return to
the bottom of the hole when the circulation is reduced or
temporarily interrupted. This property can be obtained by
utilizing additives which will impart a gel structure to the
5   drilling fluid to increase viscosities. The gel structure,
however, is preferably such that cuttings can be removed from
the drilling fluid by passing the fluid through filtration
equipment such as a shale shaker and/or sand cyclones prior to
recirculating the fluid to the drill bit. A drilling fluid must
10 also exert pressure on the surrounding formations, thus preven-
ting possible collapse of the borehole or influx of highly
pressurized oil or gas in the formation. Finally, a drilling
fluid should serve as a lubricating and cooling agent for the
drill string and the bit.

15   Drilling of easily dispersible formations such as shales,
marls and chalks often presents a problem in mud solids control.
Drilled solids disintegrate in the drilling fluid while being
transported to surface and the fines thus created are very
difficult to remove. A build-up of fines is the consequence and
20 leads to an increased viscosity of the drilling fluid and a
decreased rate of penetration of the drilling operation. Ulti-
mately mud dilution is required to recondition the mud or
drilling fluid.

Accepted methods to combat drilled solids disintegration
25 are the application of encapsulating polymers and/or inhibiting
salts. These chemicals partially prevent disintegration of
cuttings and so delay the build-up of fines. In easily disper-
sible formations however, mud dilution will be unevitable in the
end.

30   Instead of, or in addition to preventing drilled solids
disintegration, aggregation of fines could well be beneficial to
solids removal.

An objective of the present invention is to assess the
possibilities of flocculants for the improvement of solids
35 removal from drilling fluids.

In particular the removal of flocculated shale fines over sieves is an object of the present invention.

Application of coagulants and/or flocculants serve the purpose of destabilizing a suspension. Discrete aggregates are
5   formed, that are easier to separate from the fluid by settling, sieving, filtration, flotation, centrifugation or other separation methods.

The terms flocculation and coagulation are defined as follows.
10   Coagulation is used for the aggregation process, brought about primarily by a reduction of the repulsive potential of the electrical double layer of shale particles. Flocculation is used for the formation of a random loose floc structure, usually brought about by high molecular weight polymers. It should be
15   noted that some polyelectrolytes act both as a coagulant and a flocculant.

The use of ferri and aluminium salts as coagulants is known and widely applied. High molecular weight polyelectrolytes however have proven to be more efficient in many applications.
20   The choice of a coagulant and/or flocculant for improvement of a certain separation process depends on 1) the type of separation 2) type and 3) concentration of suspended solids and 4) the nature (composition) of the suspending fluid. Especially in case of polyelectrolytes, it is very difficult to base such a
25   choise on general theoretical considerations.

Solid/liquid separation with the aid of coagulants and/or flocculants is a common process in many industries, e.g. waste water treatment, water clarification, mineral ore separation, paper making, oil/water separation .... etc ...
30   The characteristic demands of drilling fluids are the following:

i <u>Selectivity</u>

Often, drilling fluids contain two types of solids; those added on purpose for increasing viscosity, fluid loss reduction and density improvement, and formation solids,

5 produced while drilling. The organic polycationic polymeric flocculant or coagulant applied according to the invention enhances the removal of drilled solids, but does not interact with soluble mud additive(s).

ii <u>Compatibility</u>

10 Soluble mud additives and flocculants and/or coagulants should be fully compatible. The flocculating properties should not be affected by mud additives and rheological and fluid loss properties not by the flocculant and/or coagulant. In the present formulation comprising high molecular weight

15 polycationic polymers, such antagonistic interaction does not exist.

iii <u>Floc strength & size</u>

Flocs are formed either downhole, where fines are created, if the flocculant is an intrinsic component of the fluid,

20 or in the flowline if the flocculant is added there at a balanced rate. In both cases a certain amount of viscous shear is exerted on the flocs. Further mechanical shear takes place on sieves (shale shakers) being used for regenerating the circulating drilling fluid. Flocculant

25 application is only successful if the flocs stay reasonably in tact during the transport and separation process.

Another important parameter is floc size. If only very small flocs are formed, a gelly-like substance is developed, plugging off the sieves. The present high

30 molecular weight organic polycationic polymeric flocculant is able to create reasonably strong and big flocs, being several millimetres in diameter.

iv   <u>Dispersion</u>

During drilling of dispersible formations, big cuttings will be produced. A flocculant should not enhance the dispersion of these cuttings and should preferably be compatible with cutting encapsulating polymers, preferably present in the drilling fluid. A combination of cutting encapsulation and fines aggregation would of course give the optimal drilling fluid for easily dispersing formations. Also erosion and/or swelling of the borehole wall should not be enhanced by a flocculant or a coagulant.

The present high molecular weight cationic polymers meet these requirements.

In principle the polycationic flocculants can be used for aggregation of many types of fine suspended solids, such as shales, marls and chalks.

Traditionally, bentonite or other clay solids have been utilized to increase the viscosity of the drilling fluid. Today however, there is a growing belief that bentonite or clay suspensions have serious limitations as a drilling fluid base. The rheology of bentonite-based fluids is such that the hydraulic horsepower delivered to the bit at a given surface pressure is significantly less than with drilling fluids containing certain polymers. The lower viscosity and/or solids content of these polymer muds result in a faster bit penetration rate which in turn decreases the drilling costs. Therefore the drilling fluid according to the invention contains at least one polymeric viscosifier including, for example: cellulose compounds such as carboxyethyl cellulose, carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose, hydroxyalkyl celluloses, alkylhydroxyalkyl celluloses, alkyl celluloses, and alkylcarboxyalkyl celluloses; polyacrylamides; natural galactomannans such as guar gum, locust bean gum, and gums derived from endosperm seeds; starches and various other polysaccharides, such as the heteropolysaccharide obtained from Pseudomonas sp. NCIB 11592,

known by its registered trade name Shellflo-S. The concentration
of the polymeric viscosifier(s) is preferably in the range from
1 to 50 g polymeric viscosifier per litre of drilling fluid.

5   As mentioned hereinbefore the drilling fluid according to
the invention contains at least one polymeric fluid loss reducer.
Suitable polymeric fluid loss reducers are (pregelatinized)
starch, gums, polyanionic cellulosic polymer, sodiumpoly-
acrylonitrile, sodiumcarboxymethyl cellulose and sodiumpoly-
acrylate. Preferably the drilling fluid contains from 1 to 50 g
10   polymeric fluid loss reducer per litre of drilling fluid.

Advantageously in the drilling fluid according to the
invention at least one encapsulating polymer is present in order
to improve the separation of fine drilled solids from the
circulating drilling fluid during the drilling operation with
15   the aid of sieves, e.g. the so-called shale shakers.

Preferably the encapsulating polymer content of the
drilling fluid is in the range from 0.1 to 10 g/litre. Examples
of suitable encapsulating polymers are hydrolyzed polyacrylamide,
polyanionic cellulose and heteropolysaccharide.

20   A very much preferred encapsulating polymer to be added to
the present drilling fluid is a heteropolysaccharide obtained
from Pseudomonas sp. NCIB 11592, known by its registered trade
name Shellflo-S.

The drilling fluid according to the invention comprises
25   basically a certain class of organic polycationic polymers. The
polymers have a molecular weight between 5×10^5 and 15×10^6.

Any suitable method of application can be used in view of
this disclosure. The essential feature is contact between the
clay particles to be treated and the polymer-containing carrier
30   fluid. A preferred carrier fluid is water or an aqueous media.
The water can contain other ingredients which do not substan-
tially interfere with dispersion or dissolution of the polymer
in the media. The water carrier may be gelled or thickened for
certain applications. Such ingredients or additives can include

salts, mineral acids, low molecular weight organic acids, cationic or nonionic surfactants (anionic surfactants can be used with a mutual solvent) or wetting agents. The organic polycationic polymer should be present in the carrier fluid in a concentration within the range of about 10 to 5000 ppm wt of organic polycationic polymeric coagulant and/or flocculant. Lower or higher concentrations can be used but are generally not practical.

A preferred aqueous carrier fluid is a saline solution containing about 0-40% salt up to about saturation limits at the applicable temperature. The preferred salt concentration is about 2-12% by weight; however, concentrations up to about 35% can be used, as well as fresh water. The salt can be an alkali metal salt, alkaline earth metal salt, ammonium salt or combinations thereof. These include the halides, sulphates, carbonates, oxides or combinations thereof. The halides of potassium, sodium, magnesium, calcium, zinc and combinations thereof are preferred due to economics and solubility. Conventional additives such as inhibitors, surfactants, coupling agents, wetting agents and others can be used where desirable and especially where the organic polycationic polymer is used with conventional treatment procedures. The drilling fluid preferably contains salts or acids which will shrink or prevent swelling.

When oil and gas wells are cased, it is necessary to perforate the casing or to drill out a section of open hole below the casing in order to complete the well and start production. A hazard in this well completion operation is that the fluid in the well bore will damage the permeability because it often rushes into the formation when it is opened up. The well can be completed as an open hole, or by perforating using shaped charges or bullets. As a component in the completion fluid, organic polycationic polymers have a purpose of preventing damage to permeability should pressure in the well be higher than formation pressure and the well fluids enter the formation.

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     The organic polycationic polymers present in the drilling
fluid according to this invention can generally be considered
quaternary polymers with nitrogen or phosphorous as the
quaternary or cationic atom with an aliphatic, cycloaliphatic or

5   aromatic chain. Trivalent or tertiary sulphur can substitute for
the quaternary nitrogen or phosphorous in the polymers. The
cationic atom to carbon atom ratio is preferably about 1:2 to
1:36 and the molecular weight is above about 1,000. Examples of
these polycationic polymers include polyethyleneamines, poly-

10   vinylpyridinium salts, or polyallylammonium salts.

     Preferred organic polycationic polymers of this invention
can be characterized and illustrated by the following formula
and examples.

$$\left[\; R_1 - \underset{\underset{R_4}{|}}{\overset{\overset{R_3}{|}}{Z}} - R_2 \;\right]_n^{+} \quad X_m^{-}$$
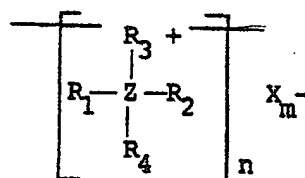
wherein

15   R_1 is an organic aliphatic, cycloaliphatic, or aromatic
radical containing 2-40 carbon atoms or a hydrogen radical and
when R_1 is cycloaliphatic Z and R_2 can be in the ring;

     R_2, R_3 and R_4 are organic radicals independently defined as
R_1 containing 0-6 carbon atoms and 0-2 oxygen or nitrogen atoms;

20   when R_1 is cycloaliphatic it may or may not be in the organic
polycationic polymer chain; when

    Z is sulphur R_4 is not present;

    Z is a cation such as those derived from nitrogen,
phosphorous or sulphur;

25   X is an anion such as halide, nitrate, sulphate, bi-
sulphate, carbonate, hydroxide, borates, oxides azides, cyanides,
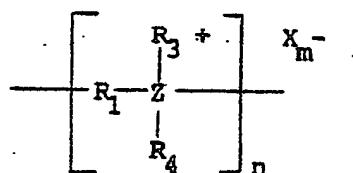phosphates, etc.;

    n is an integer equal to the number of monomer units in the
polymer required to give a molecular weight in the range of

30   about $5 \times 10^5 - 15 \times 10^6$;

m is an integer equal to the number of anions required to maintain electronic neutrality.

The organic or hydrocarbon radicals can be linear, branched or cycloaliphatic radicals, aromatic radicals, unsaturated

5 radicals, substituted radicals or combinations thereof. The organic radicals can be homoaliphatic or heteroaliphatic, i.e. may or may not contain other atoms such as oxygen or nitrogen. The organic radicals can be homocyclic or heterocyclic, i.e., may or may not contain other atoms such as oxygen or nitrogen.

10 Thus, the organic radicals can be substituted or unsubstituted alkyl, aryl or combinations thereof with each radical having 0-40 and preferably 0-6 carbon atoms.

The above class of organic polycationic polymers can be divided into the following preferred subclasses:

15 A. Alkyl Polycationic Polymers

$$\left[R_1 - \underset{\underset{R_4}{|}}{\overset{\overset{R_3}{|}}{Z}} \right]_n^{+} X_m^{-}$$

wherein

R_1 is a divalent normal or branched chain alkylene group containing 2-40 carbon atoms, preferable range 2-12 carbon atoms;

20 R_2 is contained with R_1;

R_3 is normal or branched alkyl or hydrogen containing 0-6 carbon atoms and preferably 1-3 carbon atoms;

R_4 is radical defined the same as R_3, but it may or may not be identical to R_3, e.g., R_3=methyl and R_4=propyl; when Z is

25 sulphur R_4 is not present;

Z is a cation such as those derived from nitrogen, phosphorous, or sulphur;

X is an anion such as halide, nitrate, sulphate, hydroxide, etc;

n is an integer equal to the number of monomer units in the polymer required to give a molecular weight in the range of about 5×10^5 - 15×10^6; and

m is an integer equal to the number of anions required to maintain electronic neutrality.

One preferred group of this subclass is applied in a carrier fluid at a pH greater than about 4, especially in the range of about 5-9. In another preferred group when Z is nitrogen, at least one of R_3 and R_4 is not hydrogen, methyl, ethyl or propyl.

B. Heteroaliphatic Polycationic Polymers

$$\left[\begin{array}{c} R_3 \\ | \\ R_1 - Z - R_2 \\ | \\ R_4 \end{array} \right]^+_n \quad X_m^-$$
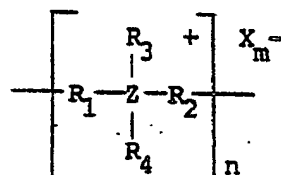
wherein

R_1 is arylene, alkylene, arylalkylene, alkylarylene, alkenylene or combinations thereof. When R_1 is alkyl it contains or has appended one or more hetero atoms or groups. When R_1 is aryl, or alkylaryl it can contain or have appended one or more hetero atoms or groups. R_1 can be normal-hetero-alkyl or it can be branched extensively through the hetero-atoms or groups. The hetero-atoms or groups may be ethylenic (-CH=CH-, acetylenic (-C≡C-), aryl, or nitrogen phosphorous, or sulphur in regular covalent bonding, partially oxidized, e.g., sulphone, or in the onium state, other hetero atoms or groups may be oxygen, hydroxyl, carbonyl, or covalent halogen. With the exception of ethylenic, or aryl, a hetero atom or group is not bonded directly to Z.

R_2 is an unsubstituted alkyl or it can be defined as R_1 but it is not required to be identical to R_1. R_2 can be included in R_1.

R_3 can be alkyl containing 1-6 carbon atoms, hydrogen or it can be defined as a monovalent form of R_1 but it is not required to be identical to R_1.

R_4 can be defined as R_3 but it is not required to be identical to R_3. When Z is sulphur R_4 is not present.

Z is a cation such as those derived from nitrogen, phosphorous or sulphur.

X is an anion such as halide, nitrate, sulphate, hydroxide etc.

n is an integer equal to the number of monomer units in the polymer required to give a polymer with a molecular weight in the range of about $5 \times 10^5 - 15 \times 10^6$.

m is an integer equal to the number of anions required to maintain electronic neutrality.

The polymer can branch through R_1, R_2, R_3, or R_4 in such manner that the main polymer chain is an arbitrary choice and R_1, R_2, R_3, and R_4 are arbitrary choices around any particular Z.

A typical branched polymer is shown as follows:
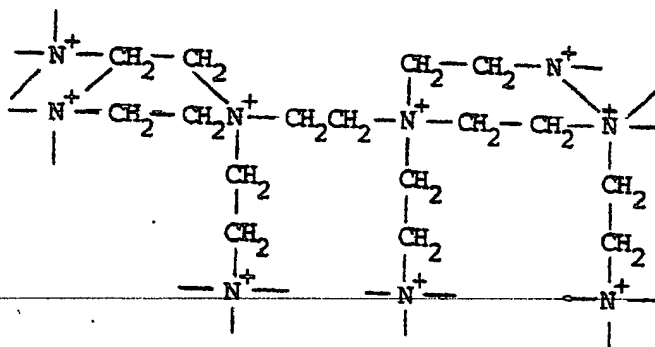
The anions are omitted for clarity.

C. Polycationic Polymers Containing Rings

$$\left[\begin{array}{c} R_1 \\ \overset{+}{\underset{R_4 \quad R_3}{\diagup Z \diagdown}} \end{array}\right]_n X_m^-$$
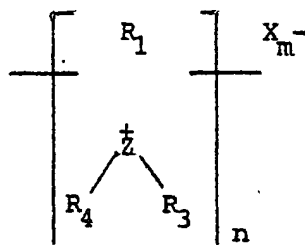
R_1 is alkylene, unsaturated alkylene, substituted alkylene, or substituted unsaturated alkylene forming a heterocyclic ring including Z. The heterocyclic ring can be aliphatic, olefinic or aromatic depending on the degree of unsaturation. Substitutions can be alkyl, alkenyl, alkynyl, or aryl branches or substitutions can be hetero atoms or hetero groups contained in the ring, appended to the ring, or appended to the branches. Hetero atoms or groups can be phosphorous or sulphur (in regular covalent, onium or oxidized state, e.g. phosphate or sulphone), nitrogen, oxygen, hydroxyl, carbonyl, or covalent halogen, a restriction being that the hetero atom or group is not bonded directly to Z.

R_2 is included in R_1.

R_3 is a hydrogen radical or an organic radical containing 1-6 carbon atoms and 0-2 oxygen or nitrogen atoms. In the case of certain aryl polycationic polymers, with monomer units bonded through Z and elsewhere on the aryl, R_3 may be absent.

R_4 is defined the same as R_3 but is not required to be identical with R_3. When Z is sulphur R_4 is absent.

Z is a cation such as those derived from nitrogen, phosphorous or sulphur.

X is an anion such as halide, nitrate, sulphate, hydroxide, etc.

n is an integer equal to the number of monomer units in the polymer required to give a polymer with a molecular weight in the range of about $5 \times 10^5 - 15 \times 10^6$.

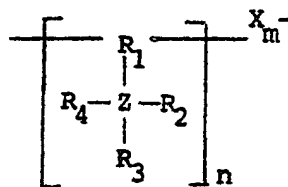m is an integer equal to the number of anions required to maintain electronic neutrality.

Bonds containing monomer units may be through Z, other hetero atoms, R_1 (1 or 2 sites), or branches on R_1.

5   ## D. Pendent Polycationic Polymers

$$\left[\begin{array}{c} R_1 \\ | \\ R_4 - Z - R_2 \\ | \\ R_3 \end{array} \right]_n X_m^-$$

wherein

R_1 can be alkylene, alkenylene, alkynylene, arylene, and linkages or branches of these in combinations. R_1 can contain hetero atoms or groups in the pendent linkage, on branch chains,

10   on or in the polymer linkage. Hetero atoms or groups can be phosphorous or sulphur (in regular covalent, onium, or partially oxidized state, e.g., sulphone), nitrogen oxygen, hydroxyl, carbonyl, or covalent halogen, a restriction being that the hetero atom or group is not bonded directly to Z. The pendent

15   linkage can range from a simple bond to branch of R_1 several atoms long connecting Z to the polymer chain.

R_2, R_3 and R_4 can be defined independently as alkyl, alkenyl, aryl or combinations thereof or can be hydrogen, except that they unlike R_1 are not in the polymer chain. When R_2 is

20   aryl including Z in a heterocyclic ring and/or when Z is sulphur R_3 or R_4 may not exist.

Z is a cation such as those derived from nitrogen, phosphorus, or sulphur. In one preferred class not more than two of the three R groups can be hydrogen. In another preferred class

25   when R_2 is aryl and contains nitrogen, the aryl ring has at least one substituent or contains one other hetero atom or group.

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X is an anion such as halide, nitrate, sulphate, hydroxide, etc.

n is an integer equal to the number of monomer units in the polymer required to give a polymer with a molecular weight in the range of about $5 \times 10^5 - 6 \times 10^6$.

m is an integer equal to the number of anions required to maintain electronic neutrality.

The following are examples of the preferred polycationic polymer classes having repeating polymer units such as those illustrated below.

(1) where Z is sulphur, a sulphonium polymer

$$\left[\begin{array}{c} \begin{array}{c} R_1 \\ | \\ S^+ \\ / \quad \backslash \\ R_2 \quad R_3 \end{array} \end{array} \quad X^- \right]_n$$
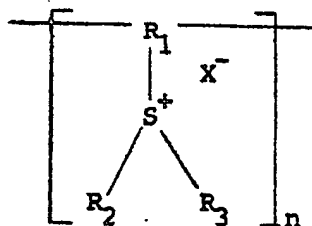
and one example is derived from the monomer $H_2C=CHCO_2CH_2CH_2S(CH_3)_2Cl$, poly-2-acryloxyethyldimethyl-sulfoniumchloride; R_1=2-acryloxyethyl, R_2=methyl, R_3= methyl, R_4=non-existent, and X=chloride.

The above formula and R groups show a polymer wherein the R groups are not hydrogen.

(2) where Z is phosphorous, a phosphonium polymer

$$\left[\begin{array}{c} \begin{array}{c} R_1 \\ | \\ R_2-P^+-R_3 \\ | \\ R_4 \end{array} \end{array} \quad X^- \right]_n$$
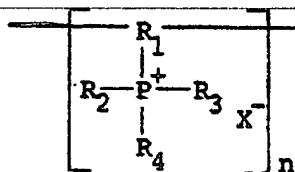
and an example monomer is

$$H_2C \overset{O}{\overset{\diagup \diagdown}{\text{———}}} CH - CH_2P(C_4H_9)_3Cl,$$

glycidyltributylphosphoniumchloride; R_1=glycidyl, R_2=butyl, R_3=butyl, R_4=butyl, and X is chloride; .

The above example shows a polymer wherein the cation Z is pendent and not in the polymer chain and at least three of the R groups are the same.

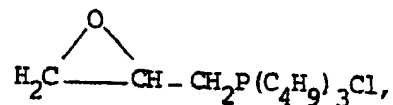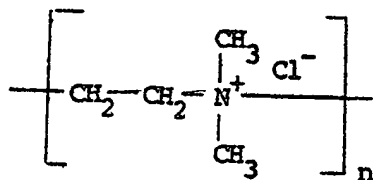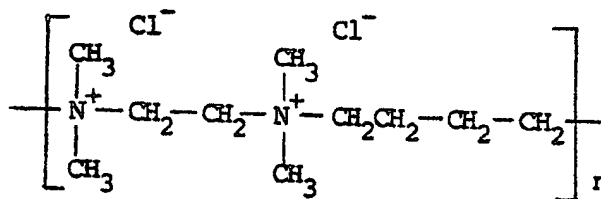(3) where Z is nitrogen, quaternary ammonium polymers;

(3a) integral alkyl quaternary, example polymer:

$$\left[CH_2{-}CH_2{=}\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{\underset{\underset{\displaystyle CH_3}{\displaystyle |}}{N^+}}\overset{Cl^-}{\text{————}} \right]_n$$

polydimethylethyleneammoniumchloride, example polymer:

$$\left[\overset{Cl^-}{\underset{\underset{\displaystyle CH_3}{\displaystyle |}}{\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{N^+}}}{-}CH_2{-}CH_2{-}\overset{Cl^-}{\underset{\underset{\displaystyle CH_3}{\displaystyle |}}{\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{N^+}}}{-}CH_2CH_2{-}CH_2{-}CH_2 \right]_n$$

the condensation product of N,N,N',N'-tetramethylethylene-diamine and 1,4-dichlorobutane.

The above examples show polymers wherein the R groups are not hydrogen; wherein the cation Z is in the polymer chain and in the second example is also in one of the R groups; wherein two of the R groups are the same and two of the R groups are different ; and wherein at least two of the R groups are linear aliphatic radicals with not more than one and/or two different radicals in the polymer chain.

(3b) Integral quaternary in cyclic ring, example polymer:
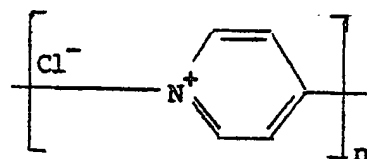
the condensation product of 4-chloropyridine;
(3c) integral alkyl, aryl quaternary, example polymer:

the condensation product of 1-(4-pyridyl)-3-chloropropane;
another example polymer:
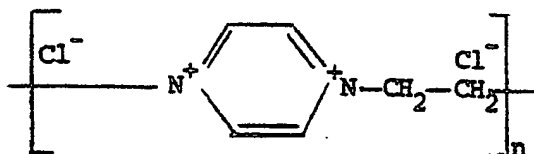
the condensation product of pyrazine and 1,2-ethylene
dichloride;

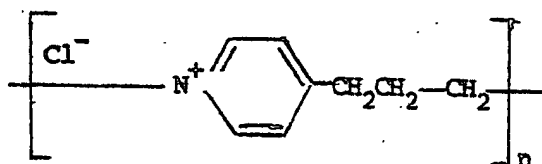The above examples show polymers with one or more cationic Z
groups in the polymer chain and in an aromatic radical which is
also in the polymer chain with two different R radicals which
are also in the polymer chain. Thus, the examples show hetero-
cyclic aromatic and linear R groups which are in the polymer
chain.

(3d) Pendent alkyl quaternary, example polymer:

$$\left[\begin{array}{c} CH_2\!-\!CH \\ | \\ N^+ \\ \diagup\ |\ \diagdown \\ CH_3\ \ CH_3\ \ CH_3 \end{array}\ CH_3OSO_3^{=}\right]_n$$
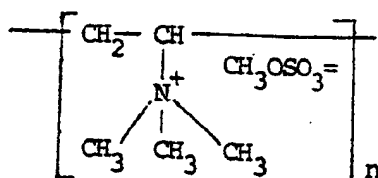
polyvinyltrimethylammonium methylsulphate.

The above example shows a polymer with a pendent cationic Z
radical and pendent R groups which are the same but different
from the R group in the polymer chain; thus, Z and three of the
R groups are not in the polymer chain.

(3e) Pendent quaternary on cyclic backbone, example polymer:

$$\left[\begin{array}{c} \\ CH_2 \\ | \\ N^+\quad Br^- \\ \diagup\ |\ \diagdown \\ CH_3\ \ CH_3\ \ CH_3 \end{array}\right]_n$$
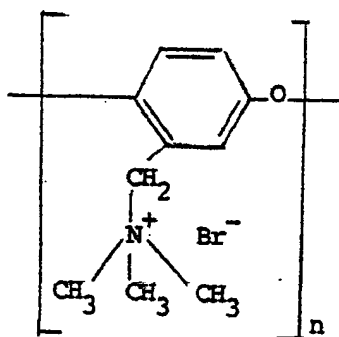
The above example shows a polymer with aromatic and hetero-
radicals in the polymer chain, a pendent cationic Z radical and
three R groups which are aliphatic and not hydrogen or not in
the polymer chain.

(3f) Pendent quaternary on carbocyclic ring, example polymer:

$$\left[\begin{array}{c} CH_2\!-\!CH \\ | \\ \bigcirc \\ | \\ CH_2 \\ | \\ H_3C\!-\!N\!-\!CH_3 \qquad Cl^- \\ | \\ CH_3 \end{array}\right]_n$$
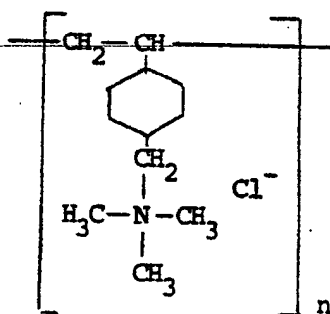
polyvinyl-4-benzyltrimethylammoniumchloride;

(3g) Pendent quaternary nitrogen on polymethacrylate backbone, example polymer:

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ C=O \\ | \\ O \\ | \\ CH_2-CH-CH_2-\overset{+}{N}-CH_3 \\ \quad\quad | \quad\quad\quad | \\ \quad\quad OH \quad\quad CH_3 \end{array} \right]_n \quad Cl^-$$
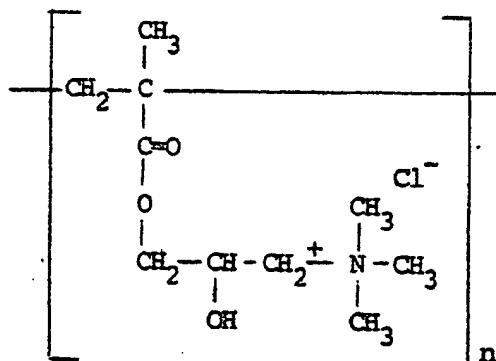
poly(3-methacryloxy-2-hydroxypropyltrimethylammonium
5   chloride).

The above example shows different R groups with one in the polymer chain and three aliphatic R groups with one containing a cationic Z group and hetero atoms which are not in the polymer chain.

10   Another example polymer:

$$\left[\begin{array}{c} -CH_2-CH- \\ | \\ C=O \\ | \\ H-N-CH_2-CH_2-CH_2 \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad \overset{+}{N} \quad Cl^- \\ \quad\quad\quad\quad / \; | \; \backslash \\ \quad\quad CH_3 \; CH_3 \; CH_3 \end{array} \right]_n$$
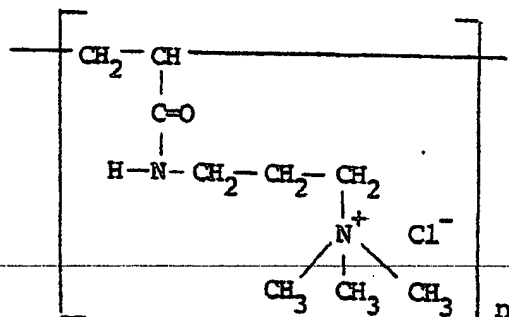
poly(acrylamide-3-propyltrimethylammoniumchloride).
The above example shows a polymer with pendent R groups and cations which are not in the polymer chain, aliphatic R groups with one in the polymer chain, and a pendent group containing
15   hetero atoms and more than one Z group.

(3h) Quaternary nitrogen in pendent heterocyclic ring, example polymers:

$$\left[\begin{array}{c}CH_2-CH \\ \big| \\ \text{(pyridinium ring)} \\ N^+ \\ I^- \quad CH_3\end{array}\right]_n$$

poly-4-vinyl-N-methylpyridiniumiodide;

The above formula shows a polymer with a pendent hetero aromatic

5   radical which is also a cationic radical and they are not in the organic polycationic polymer chain.
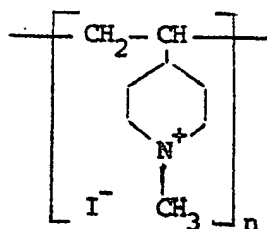
(3i) Heterocyclic ring containing quaternary nitrogen, example polymers:

$$\left[\begin{array}{c}CH_2 \\ CH \qquad CH-CH_2 \\ CH_2 \qquad CH_2 \\ N^+ \quad Cl^- \\ H_3C \qquad CH_3\end{array}\right]_n$$

$$\left[\begin{array}{c}CH_2-CH \qquad CH-CH_2 \\ CH_2 \qquad CH_2 \\ N^+ \quad Cl^- \\ CH_3 \qquad CH_3\end{array}\right]_n$$
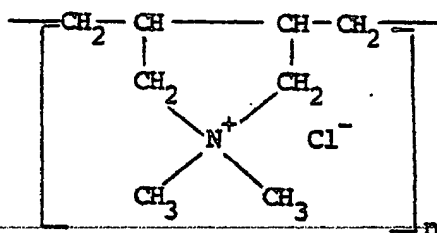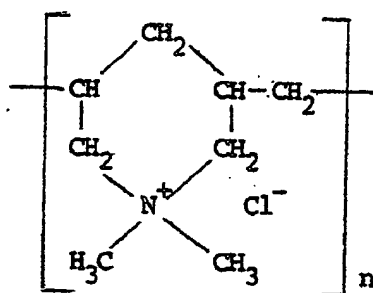
polymer of diallyldimethylammoniumchloride.

10   The above formulae show a pendent Z cation and pendent aliphatic R groups with at least two of the R groups having the same number of carbon atoms and with two R groups having the same

number of carbon atoms and being linear aliphatic radicals in
the polymer chain. The formulae also show heterocyclic aliphatic
groups in the polymer chain which also have pendent portions.

5   The above classes and subclasses of polycationic polymers
can be substantially linear or branched. Examples (3a), (3b) and
(3c) can be considered substantially linear polymers. Examples
(1), (2), (3d), (3e), (3f), (3g), (3h) and (3i) can be considered
branched. These examples show branching through at least one
organic radical such as examples (1), (2), (3d), (3e), (3f),
10   (3g), (3h) and (3i) and through a cation radical such as example
(3a). Also examples (3d), (3e), (3f), (3g), (3h) and (3i) can be
considered to have branching through pendent cation radicals or
hetero groups.

The drilling fluid according to the invention can also be
15   used as completion fluid or workover fluid.

The following example serves to illustrate various embodi-
ments of the invention and enable one skilled in the art to
practice this invention.

EXAMPLE

20   A number of flocculants were tested in various concen-
trations, in solutions of viscosifiers and fluid-loss reducers.
Qualitative tests were carried out in measuring cyclinders,
noting:
   - occurrence of flocculation and type of floc
25   - settling of the flocs
   - turbidity of the supernatant.

The results of these tests were used for primary screening
of flocculants. The best performing flocculants were used for
further testing. Suspensions were flocculated and moderately
30   sheared by hot rolling or peddle stirring for two hours. Subse-
quently the flocs were sieved off and dried, and the recovery
determined. Tests were done in solutions of single additives and
mixed solutions of viscosifiers and fluid-loss reducers.

The effect of flocculant and shale fines concentration was extensively evaluated in Shellflo-S solutions (Shellflo-S is a registered trade mark). A number of tests was carried out to compare the effect of flocculants in fresh water and KCl, NaCl and $CaCl_2$ solutions, containing Shellflo-S.

The combined effect of encapsulating and flocculating polymers was investigated in suspensions of shale fines and cuttings.

In all tests dispersed, flocculated or encapsulated shale was removed from the suspension over either 150 or 180 μm sieves and the fraction retained on the sieves was determined.

In the flocculant depletion tests, the thus obtained filtrate was again used as flocculating mud.

The shale used in all tests, either as fines or cuttings, is Pierre shale, an outcrop material from Utah (U.S.A.). Table 1 shows the composition of this shale. Table 2 summarises all flocculants used with suppliers and, if known, a description of their chemical nature.

In Table 3, a summary is given of all mud additives used, again also mentioning suppliers and chemical compositions.

Table 4 shows the results of tests on the compatibility of flocculants and coagulants, with mud additives. Incompatibility (precipitation) with some of the mud additives is considered to be too risky for a chemical to be incorporated in drilling fluids that will be used on a routine basis.

Table 5 gives the results of measuring cylinder flocculation tests. It shows which mud additive/flocculant combinations are able to flocculate a Pierre shale suspension and which are not.

The anionic flocculant SS-100 (hydrolysed polyacrylamide) shows a poor performance.

From Table 5 can be concluded that the cationic XZ-86243 performs very well.

Table 6 shows the recovery of Pierre shale fines over 100 mesh sieves. The main conclusion from these results is that a

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significant improvement in solids removal can be attained by addition of a cationic high molecular weight flocculant.

Table 7 shows the results of flocculation tests in various fluids. Since it was known in this stage that anionic polymers perform poorly, they were excluded from this test series. More cationic polymers were included instead.

The presence of salts alone, did not cause flocculation. The main conclusions are:

- The low (MW<50,000) and medium (50,000<MW<500,000) molecular weight flocculants (C 581, P.P.C.) show a poor performance in all solutions. High molecular weight ($5x10^5$<MW<$15x10^6$) is clearly required for effective solids removal improvement.

- The nalco flocculants 4625, 4725 and 4780, although used in combination with an activator are ineffective in fresh water but perform well to excellent in brines.

- For use in drilling operations XZ-86243 is preferred for fresh water systems; Nalco 4625 and 4780 (and perhaps others from this product series) for brines and C-420 for both.

Table 8 shows the effect of the flocculant concentration on solids removal for C-420, XZ-86243 and Nalco 4625. C-420 is effective, in the whole range from 10 to 1000 ppm wt; XZ-86243 shows increasing performance with increasing concentration. The water content of the retained fines clearly increases with flocculant concentration for the two effective products. This information is of particular relevance for solid waste disposal.

Variation of the fines content from 0.1 to 5.0% w/v had no effect on recoveries. Addition of 500 ppm C-420 and XZ-86243 to Shellflo-S/Pierre shale suspensions always resulted in a recovery between 90 and 100%.

In most tests viscosities of solutions with and without flocculant were measured and also the viscosity of the filtrate. Addition of up to 500 ppm flocculant always caused a slight

change in rheology, but never more than approximately ± 5%. The
viscosity of the filtrates was generally lower than that of the
initial mud, but always within a range of approximately 10%.
Taking the high solids load and normal adsorption of polymeric
5 mud additives into account, this value is according to expec-
tation.

Table 9 shows the results of combined application of
cutting encapsulators and flocculants on fines and cutting
recovery. Clearly no antagonistic effect occurs between the two.
10 Again XZ-86243 shows to be a very effective flocculant and
Shellflo-S and SS-100 excellent cutting inhibitors.

Table 10 shows the results of the triaxial shale tests c.f.
Darley, H.C.H., "A Laboratory Investigation of Borehole
Stability" J. Pat. Tech., July 1969, 883-893 AIME, 246. The
15 cationic flocculant XZ-86243 is clearly shown to be inert as far
as borehole stability is concerned.

TABLE 1 - Composition of Pierre shale

fraction < 2 um: 53.6% (= clay content)

Composition of the clay fraction	
montmorillonite	40% w/w
mixed layers	0 "
illite	50 "
chlorite	5 "
kaolinite	5 "

TABLE 2 - Description of flocculants and coagulants

Product	Supplier	Charge*	Mol. weight	Description
SS-100	I.D.F.	—	high ($>\frac{1}{2}.10^6$)	30-40% Hydrolysed polyacrylamide
XZ-86243	Dow. Chem.	++	"	Polyacrylamide with quarternary ammonium groups
C-420	Cyanamid	+	"	Polyacrylamide with cationic groups
C-436	"	++	"	"
C-461	"	+++	"	"
C-470	"	+++	"	"
C-581	"	+	medium**	Amine condensation polymer
Nalco-4625	Nalco	+	high ($>\frac{1}{2}.10^6$)	Cationic polymer
Nalco-4780	"	+++	"	"
Nalco-4725	"	++	very high ($>10^6$)**	"
P.P.C.	EGA(Aldrich)	+++	medium**	Poly(n,n-dimethyl-3,5-dimethylenepiperidiniumchloride
CP-35	Dow. Chem.	++	high ($>\frac{1}{2}.10^6$)	Modified cationic polyacrylamide
CP-50	"	++	"	"

* -/+ indicate sign and relative Density of the charge

** 50,000<MW<500,000

TABLE 3 - Description of mud additives

Mud additive	Description
Floogel	starch
Stabilose	slightly carboxylated starch
CMC	carboxy methyl cellulose
HEC	hydroxy ethyl cellulose
Drispac	polyanionic cellulose
Shellflo-S	polysaccharide (succinoglycan)

TABLE 4 - Results of mud additives/flocculant compatibility

	flocculant/coagulant		
Mud additive	SS-100	CP-35	XZ-86243
Stabilose (10) *	+	+	+
HEC (4)	+	+	+
CMC-HV (10)	+	+	+
Shellflo-S (1)	+ ,	+	+
SS-100 (2)	+	+	+
Drispac (10)	+	+	+

* between brackets: mud additive concentration in g/litre

+: compatible

- flocculants were tested in 10, 100 and 1000 ppm wt concentrations

<u>TABLE 5</u> - Flocculating efficiency of various flocculants in
<u>mud additive solutions (measuring cylinder tests)</u>

	flocculant (500 ppm wt)		
Mud additive	SS-100 (anionic)	CP-35 (cationic)	XZ-86243 (cationic)
Water	+	+	+
Stabilose (10)*	-	+	+
Floogel (10)	+	+	+
CMC-HV (10)	-	-	+
CMC-LV (10)	-	-	+
HEC (1)	-	+	+
Drispac (5)	-	-	+
Enorflo-S (1)	-	+	+

+ = flocculating

- = not flocculating

* Between brackets: concentration in g/litre

TABLE 6 - Recovery of Pierre shale fines by means of flocculants

| Mud additive | RECOVERY (%) OVER 100 mesh SIEVE | |
	No flocculant	XZ-86243 500 ppm wt
Stabilose (1) [*]	36	78
Flocgel (1)	26	65
CMC-HV (1)	27	99
CMC-LV (1)	26	97
Drispac (0.5)	46	98
Enorflo-S (0.1)	41	96
HEC (0.4)	88	93
Stabilose (1) ⎫ CMC-HV (1) ⎭ [**]	38	83

[*] = between brackets: concentration in % w/w.

[**] = flocculant concentration = 100 ppm wt
      fines concentration 40 g/l

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TABLE 7 - The effect of flocculants on recovery of Pierre shale fines over 80 mesh sieves

Flocculant	no salt	RECOVERY OVER 80 mesh SIEVES (180 μm)			
	0	no salt	NaCl (10 %wt)	KCl (10 %wt)	CaCl₂ (10 %wt)
		500 ppm wt	500 ppm wt	500 ppm wt	500 ppm wt
C-420	35	94	88	81	92
C-436	-	69	65	65	70
C-461	-	x	64	55	58
C-470	<10	88	76	49	61
C-581	<10	x	26	27	39
Nalco-4625	<10	10	99	99	99
Nalco-4725	<10	<10	69		73
Nalco-4780	2	11	91	95	89
XZ-86243	2	94	73	56	70
P.P.C.	<10	x	30	33	43

base mud: - fresh water
- 3 g/litre Shellflo-S
- 50 g/litre fines

- : no data available

x : incompatible; precipitation of polymer

TABLE 10 - The effect of the cationic flocculant XZ-86243 on borehole stability in a reconstituted Pierre shale sample

Additive	Erosion (%)	Failure time (min)	Failure type
-	17	599	collapse
XZ-86243 (0.2%)	19	705	"
XZ-86243 (0.2%) + KCl (10%)	5	no failure	no failure

confining pressure: 225 bar.

base mud: 10 g/l CMC-LV (low-viscosity carboxymethylcellulose) + 10 g/l CMC-HV (high-viscosity carboxymethylcellulose)

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C L A I M S

1. A drilling fluid comprising:
a) at least one polymeric viscosifier
b) at least one polymeric fluid loss reducer
c) at least one high molecular weight organic polycationic
polymeric coagulant and/or flocculant.

2. A drilling fluid as claimed in claim 1 in which from 1 to 50 g polymeric viscosifier is present per litre of drilling fluid.

3. A drilling fluid as claimed in any one of the preceding claims in which from 1 to 50 g polymeric fluid loss reducer is present per litre drilling fluid.

4. A drilling fluid as claimed in any one of the preceding claims in which from 10 to 5000 ppm wt of high molecular weight organic polycationic polymeric coagulant and/or flocculant is present.

5. A drilling fluid as claimed in any one of the preceding claims in which at least one encapsulating polymer is present.

6. A drilling fluid as claimed in claim 5, in which from 0.1 to 10 g encapsulating polymer is present per litre of drilling fluid.

7. A drilling fluid as claimed in claim 1, substantially as described hereinbefore with special reference to the Example.

8. A process for drilling, completing or working over a well in an underground formation in which process a drilling fluid as claimed in any one or more of the preceding claims is circulated.

DWRH04/MF